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Mechanisms of Polymer Degradation Using an Oxygen Plasma Generator

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INTRODUCTION

A study was initiated to determine whether or not the Plasma Prep II oxygen plasma generator could be used to produce polymer degradation or erosion similar to that which has been observed with Kapton, Mylar, Tedlar, and Teflon films in low earth orbit (LEO) * (References 1 through 11). The Plasma Prep II is a low cost atomic oxygen plasma generator system which can be used for cleaning organic residues from ceramics and electronic parts as well as for other oxygen reaction experiments. This system has been used previously to study degradation of spacesuit materials (Reference 13). It consists of a chamber with an RF generator (13.56 MHz; 0 - 100 watts) and operates in a dynamic oxygen atmosphere at 200-500 mTorr. The plasma which is generated is nonuniform in density, is not unidirectional, and may vary in energy from one to several hundred eV (Reference 13). Attempts to calculate these parameters for comparison with orbital conditions are unrealistic, but it is apparent that much higher fluxes and energies are produced in localized regions of the generator than those found in low earth orbit. According to the manufacturer (SPI Supplies, Inc. West Chester, PA), the physical process involves the production of electrons by ionization followed by an increase in energy in the electric field. "Subsequent collisions between the energetic electrons and neutral gas molecules result in an energy transfer to the molecules producing chemically active atoms, free radicals, ions, and free electrons." (Reference 12.) Reaction products resulting from interaction of the plasma with sample materials are carried away in the gas stream. A unique property of this process is that it occurs with the material near ambient temperatures. Preliminary experiments showed that Kapton is significantly degraded by exposure to the plasma in this apparatus. The observed damage to the Kapton seems analogous to that which occurs in orbit in several respects. There was substantial weight loss; the visible appearance of the damaged surface was similar; surface morphology, as shown by scanning electron microscopy (SEM) at 1250 X, showed similar eroded channels; and pyrolysis mass spectrometry of degraded surface material gave the same result as for orbit degraded material (no new surface structure was developed). The biggest discrepancy, however, was the fact that the damage showed a high degree of nonuniformity and variability. This characteristic severely limits the use of this apparatus for quantitative correlations of the amount of damage as a function of time, dose, or type of material.

Because of the qualitative similarities, it seems appropriate to suggest that the molecular mechanisms responsible for the plasma-induced degradation might be similar to those involved in the LEO degradation. If this is true, then studies of mechanisms using the plasma generator may

properly be related to mechanisms of the analogous phenomena in LEO.

As in any investigation of the mechanisms of a chemical reaction, in this case too, it is vital to identify the products of the reaction before a clear understanding of the phenomenon can be achieved. The plasma generator system is especially amenable to such analyses since the by-products are swept out by the dynamic flow of oxygen through the system. In the present study, those by-products have been cryogenically trapped and subsequently identified by infrared, mass spectral, x-ray diffraction, or GC/MS techniques. Weight loss measurements were made on the polymer samples and surface morphology studies were obtained from the SEM.

UNIQUE APPARATUS AND EXPERIMENTAL PROCEDURE

In order to trap the volatile species which evolve during a degradation experiment, a liquid nitrogen cold trap was designed and built into the exhaust port of the generator (Figure 1). Initially the trap was made of copper tubing (later replaced with pyrex) and was valved on each end so that it could be removed at the conclusion of a degradation experiment and coupled directly to the analytical mass spectrometer (Hitachi RMU-6) for analysis of collected volatile materials. Analyses of liquid or solid products which collected in the trap were accomplished by rinsing out with appropriate solvents and analyzing the resulting residues after evaporation. Pyrolysis mass spectrometry, gas chromatography mass spectrometry (GC/MS), infrared spectrophotometry, and x-ray diffraction techniques were invoked according to the nature of the sample.

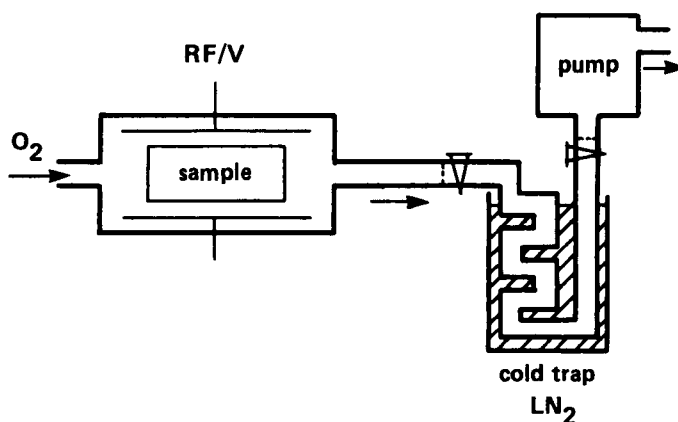


Figure 1. Plasma generator/trapping system.

EXPERIMENTAL RESULTS

Preliminary exposures of Kapton (polyimide film) in the Plasma Prep II chamber showed that significant degradation did in fact occur within 1 or 2 hours. The damage was extremely nonuniform, with some areas apparently unaffected and some completely eroded away (Figure 2). The physical appearance of the degraded portion was similar to that of Kapton which had been degraded in orbit. That is, the natural luster of the yellow-brown polymer was changed to a diffuse dusty-white appearance. Scanning electron microscope images at 5000 X showed a morphology strikingly similar to that of many polymer samples damaged by atomic oxygen in orbit (Figure 3). Substantial weight loss was recorded in all cases averaging 45 mg/hr for Kapton (samples were approximately 100 cm² in total area, but much of the surface remained undamaged) and pyrolysis mass spectrometry of the degraded surface material gave similar results in both cases.

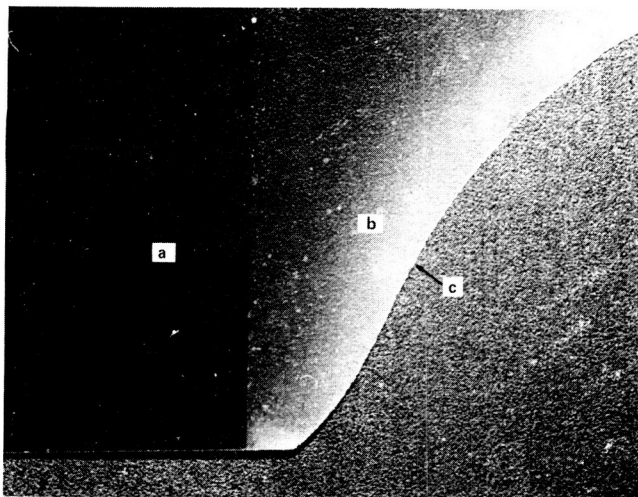
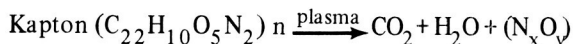


Figure 2. Degraded Kapton.
a. Masked Area (unaffected)
b. Degradation Gradient
c. Edge of Completely Eroded Area

The initial analysis of collected gaseous products from Kapton showed that a considerable amount of carbon dioxide, some water, and possible traces of nitrogen oxides had been produced. There was no evidence of any organic fragment species!



This result is somewhat surprising since it indicates complete combustion and provides little information regarding mechanisms. Consequently, some other types of polymers were chosen and subjected to plasma degradation in order

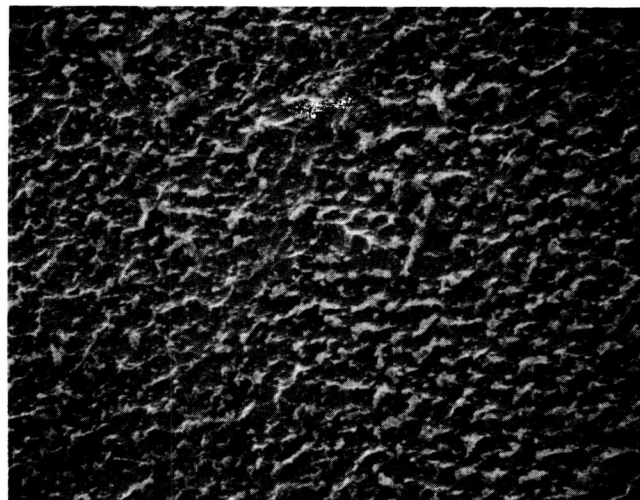
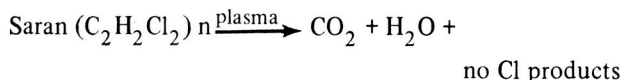


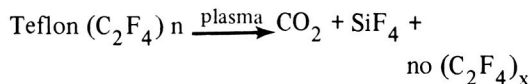
Figure 3. Plasma Degraded Kapton.
SEM Micrograph—5000 X

to attempt to gain more insight regarding the processes of reaction. Chlorinated and fluorinated polymers (Saran-polyvinylidene chloride and Teflon-polytetrafluoroethylene) were chosen in order to get explicit information by identifying the expected halogenated products.

The results for Saran were somewhat disconcerting since neither chlorinated vapors nor organic fragments could be detected even though substantial weight loss did occur. Only carbon dioxide and water were found by the gas analysis.



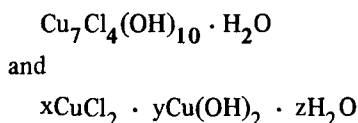
The result with Teflon was even more unexpected. A large amount of silicon tetrafluoride gas was found along with about an equal amount of carbon dioxide.



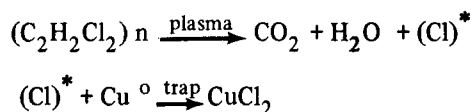
Again no products relating to the polymer structure, such as tetrafluoroethylene, could be detected. Since the only possible source of silicon in the entire system is the pyrex reaction chamber housing, it is apparent that the plasma reaction liberated a reactive fluorine entity from the polymer which subsequently reacted with the glass chamber wall to produce the volatile SiF₄ species which was collected in the cold trap.

When a methyl silicone polymer film (DC 93-500) was exposed in the plasma generator for 2 hours, no weight loss was detected. In this case, no attempt was made to analyze for possible products.

The next task was to find out what happened to the chlorine component from the Saran. After studying the boiling point behavior of possible products (Figure 4), it was apparent that none of them containing chlorine could escape through the cold trap (all would be condensed at -195°C). Subsequent rinsing of the copper trap with ethanol removed 6 mg of a green crystalline material which was identified by x-ray diffraction as cupric chloride (CuCl_2). Further rinsing of the trap with distilled water resulted in significant amounts of yellowish-green material which was identified as mixed hydroxy chloride salts of copper including:

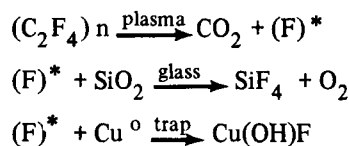


These results show that a reactive chlorine entity was liberated from the Saran polymer, was carried into the cold trap, and reacted with the copper metal. The overall reactions could then be represented as follows:



Calculations showed that about one-third of the weight of chlorine which was lost during exposure was ultimately recovered in the form of copper salts in the cold trap.

Further experiments using the same trapping system, but with Teflon instead of Saran, produced significant amounts of a robin's-egg-blue crystalline substance in the copper trap which was identified as cupric hydroxyfluoride. This identical product was found using both polytetrafluoroethylene (PTFE) and polyfluorinated ethylenepropylene (PFEP), and SiF_4 gas was found in both cases. The reactions can then be represented as follows:



If there was any F_2 gas produced during this reaction, it would probably not be retained in the trap (bp = -188°C) and one possible oxygen product, OF_2 , (bp = -145°C) might escape while CF_4 (bp = -128°C) should be condensed. None of these was detected. None of the possible chlorine species which might be derived from the Saran degradation is sufficiently volatile to pass through the trap.

BOILING POINTS OF POSSIBLE PRODUCTS

H_2	-253°C	CH_3F	-82°C
N_2	-196	C_2F_4	-76
CO	-192	$\text{C}_2\text{H}_3\text{F}$	-72
F_2	-188	CH_2F_2	-52
O_2	-183	$\text{C}_2\text{H}_5\text{F}$	-38
CH_4	-164	Cl_2	-35
NO	-152	$\text{C}_2\text{H}_4\text{F}_2$	-25
OF_2	-145	CH_3Cl	-24
CF_4	-128	Si_2OF_6	-23
O_3	-112	Si_2F_6	-19
C_2H_4	-104	CH_3ONO	-12
N_2O	-89	CH_3NH_2	-6
C_2H_6	-89	$\text{C}_2\text{H}_5\text{Cl}$	$+12$
SiF_4	-86	$\text{C}_2\text{H}_5\text{O}$	$+13$
HCl	-85	HF	$+20$
$\text{C}_2\text{H}_2\text{F}_2$	-83	NO_2	$+21$
CHF_3	-82		
C_2H_6	-79		
CO_2	-79		

Figure 4

The next experimental phase was developed to try to learn more about the nature of the reactive chlorine and fluorine species which are derived from the plasma degradation reactions. A new cold trap made of pyrex was used in order to avoid reactions with the copper, and the Teflon, Saran, and Kapton experiments were repeated. The results in each case were much more ambiguous than anticipated. From the Saran, a mixture of chlorinated solids was obtained and no positive identification of individual species could be made. Similarly, a fluorinated mixture was obtained from the Teflon. Solids in this mixture decomposed at 170°C to yield silicon tetrafluoride. Degradation of Kapton resulted in small amounts of solid nitrogen containing compounds (amines or amides) which were also very difficult to analyze.

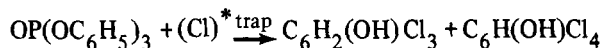
In order to allow for a more positive scheme of analysis of secondary reaction products, it was decided to coat the inside of the cold trap with an organic free radical scavenger. This material was chosen primarily because the products of its reaction with the expected reactive species (free radicals) could be readily separated and analyzed by GC/MS techniques. The material chosen was triphenyl phosphate

(TPP) which has a boiling point of 245°C and is readily chromatographed using column conditions appropriate for vacuum condensable materials. This combination of properties assures that the scavenger will not be lost during the vacuum operations required for the degradation experiment and that the expected products will give positive and satisfactory analytical results.

The results using TPP in the cold trap during plasma degradation of Saran were informative and indicative of the reactive nature of the plasma-induced products. Figure 5 shows a reconstructed gas chromatogram of the secondary products created in the cold trap during a 4-hour Saran/plasma degradation experiment. Identification of the various species was accomplished by mass spectral matching and retention time characteristics and includes many fragmentation and chlorination products. The wide variety of types of products indicates the very reactive nature of primary degradation species condensed on the TPP in the cold trap. The production of chlorotriphenyl phosphate seems to be the only straightforward reaction occurring in the trap.

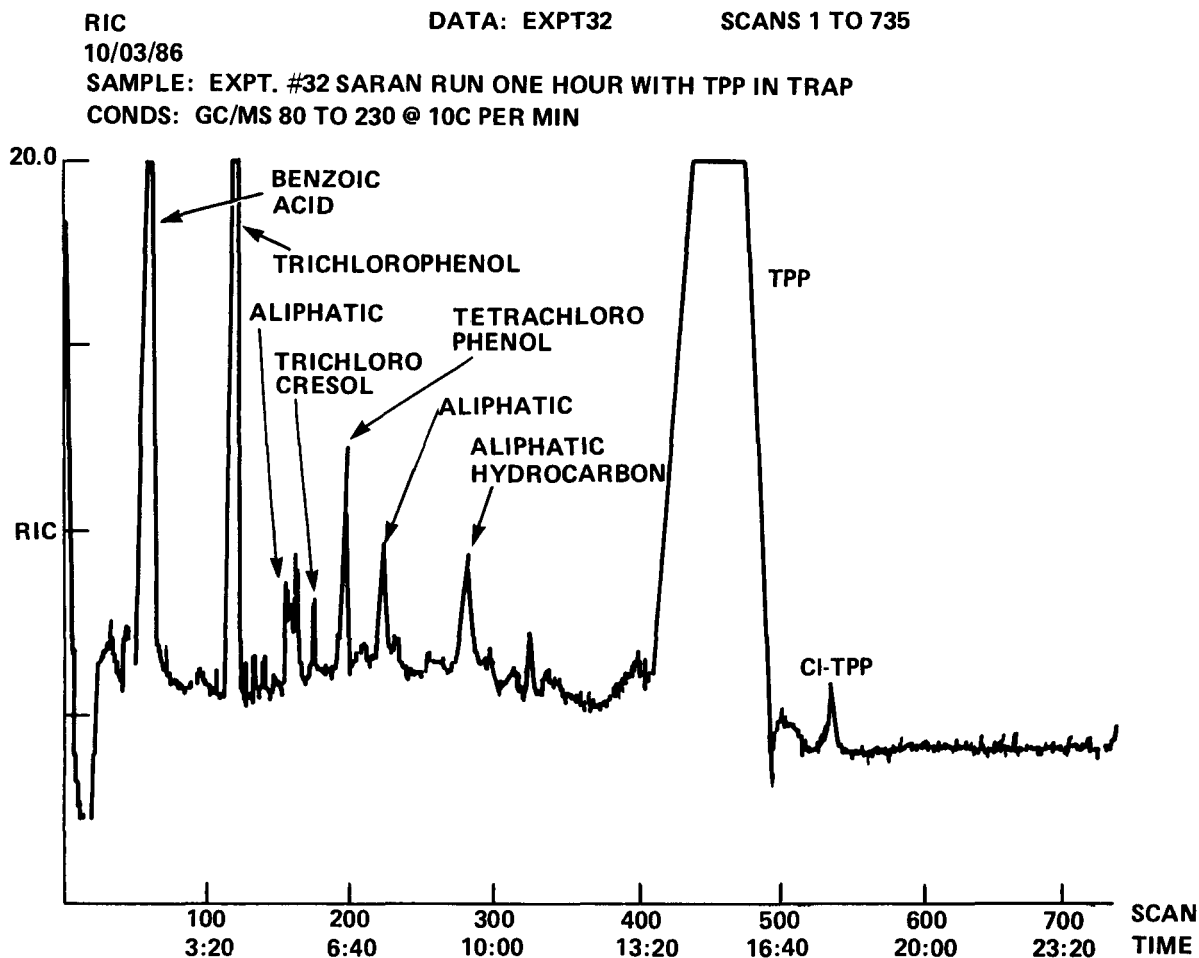


The chlorophenol compounds must result from scission of the phenyl group from the TPP followed by multiple chlorination reactions.



More complicated reactions must be postulated to explain the production of benzoic acid and trichlorocresol while complete destruction of the normally stable aromatic unit would be required to produce the aliphatic compounds.

Similar experiments with the TPP scavenger in the trap were conducted using Teflon and Kapton in the plasma reaction vessel. Again, complicated and varied products were identified as shown in the chromatograms in Figures 6 and 7. From the Teflon experiment, benzoic acid and aliphatic products were identified as well as a larger molecular weight compound related to TPP but not found in our libraries and not readily identified. No fluorinated products were confirmed except for the SiF_4 in the gas phase. From



Kapton, the destruction of the TPP was again demonstrated, as well as formation of traces of ring compounds containing nitrogen which could have arisen either as direct degrada-

tion products from the Kapton or as products of reactive nitrogen interaction with the TPP.

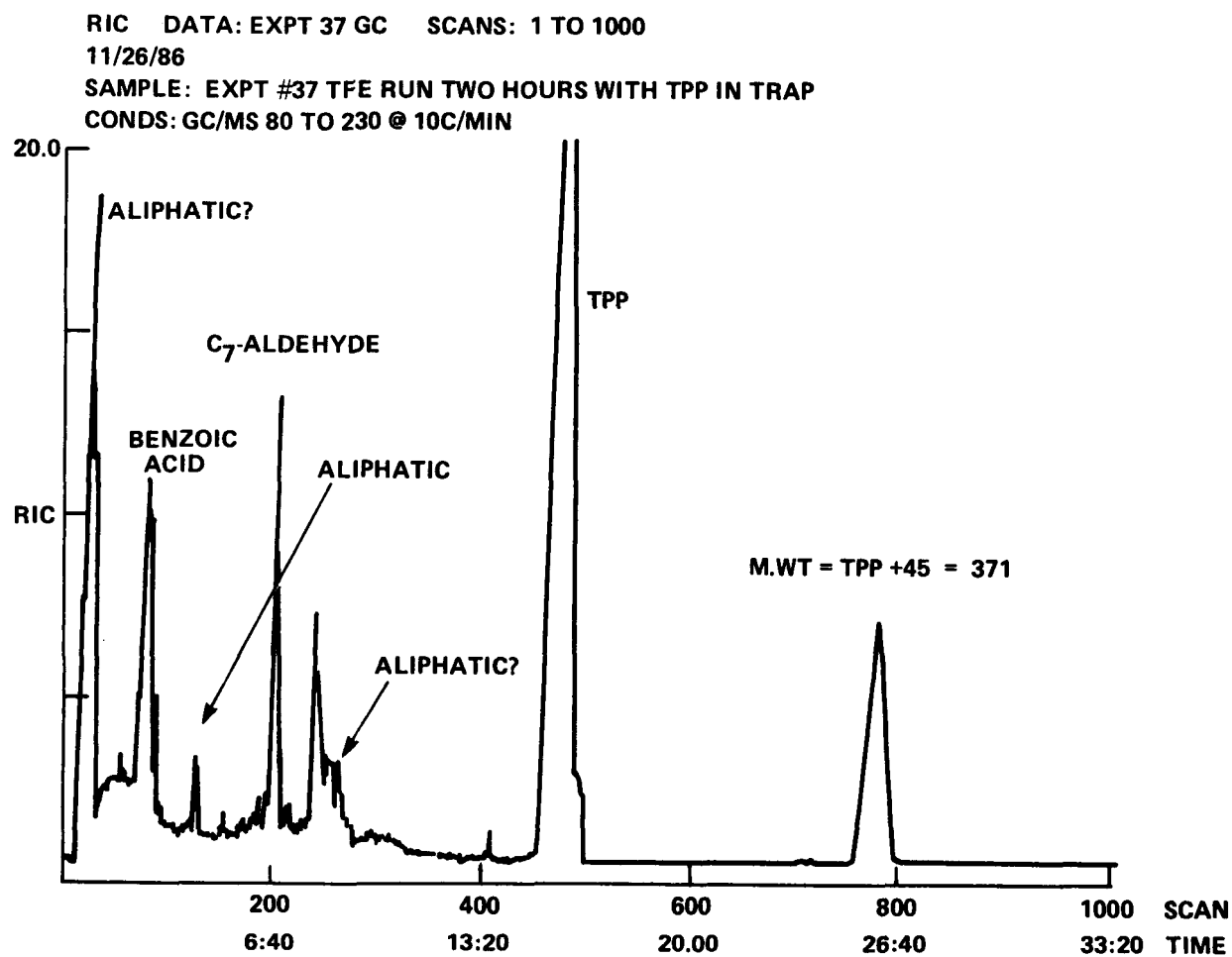


Figure 6.

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SAMPLE: EXPERIMENT #38 KAPTON 4-HOUR-RESIDUE FROM TPP TRAP

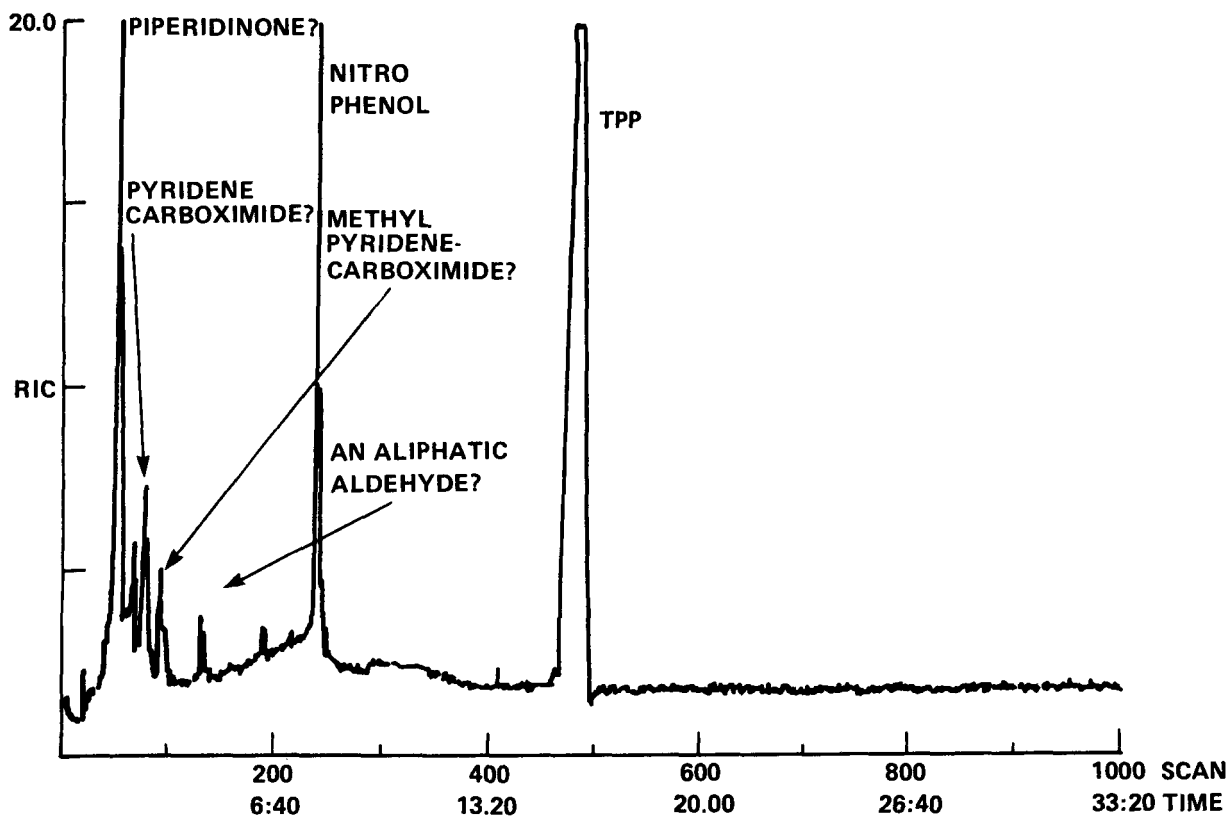


Figure 7.

DISCUSSION AND CONCLUSIONS

It has been shown that exposure in the plasma generator causes degradation of Kapton, Teflon, and Saran but not of methyl silicone films. The primary reaction products were shown to be carbon dioxide, water, and a variety of extremely reactive free radical entities depending on the elemental composition of the polymer. The reactivity of the free radicals is attested to by the formation of silicon tetrafluoride from reaction of the fluorine radical with the pyrex chamber wall; by the formation of copper halogen salts in the trap by reaction of chlorine or fluorine radicals with copper metal; and by destruction of the triphenyl phosphate molecule in the trap by reactive species from all three types of polymers. The exact nature of these free radicals is still a matter of conjecture, but their reactivity is certain. Another important experimental result demonstrated by this work is the fact that no fragment species related to polymer structure were identified in any of these samples. This is in contrast to thermal degradation in vacuum

which generally produces structurally related products such as tetrafluoroethylene from Teflon.

If these results have any validity in terms of correlation with low earth orbit degradation processes, then a number of practical recommendations regarding usage of flight materials should be considered. For long term exposure such as on the Hubble Space Telescope or on Space Station structures, concern about possible changes in the properties of exposed materials is certainly valid. However, it may also be important that we consider the fate of reactive material which may be liberated during atomic oxygen interaction with exposed polymeric materials. If the glass plasma generator chamber can be attacked at room temperature and cryogenically-trapped free radicals can react with copper and triphenyl phosphate, then these same type of radicals can attack adjacent flight structures of components during orbital exposure.

In order to establish the validity of the postulate that mechanisms of degradation in LEO are similar to those occurring in the plasma generator system, a flight experiment based on the same scheme of analysis is being proposed for a Shuttle flight. This experiment would expose materials in such a way that the products could be cryogenically trapped and returned to the laboratory for chemical analysis. Correlation of the results should demonstrate the validity of this experimental approach as well as adding a vital dimension to our understanding of materials interactions with the LEO environment.

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